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DEVELOPMENT OF PORTABLE INSTRUMENTATION FOR MEASUREMENT OF CARBON MONOXIDE AND NICOTINE

Final Report

March 1980

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I INTRODUCTION

SRI International was requested to develop an unobtrusive instrument package for the analysis of atmospheric carbon monoxide (CO) and nicotine. This instrument system must be portable, self-contained, and operable by personnel with a minimum of specialized training. A prime requirement for the instrument system is that the data obtained be credible beyond reasonable criticism.

This research program included the development, testing, evaluation, and verification of the accuracy of an instrument system to measure CO and nicotine under realistic conditions. Two of these instrument packages have been assembled and tested by measuring actual field concentrations in public and semi-public places.

The instrument system must be unobtrusive to produce unbiased measurements of CO and nicotine. For example, measurements made inconspicuously can prevent situations in which people could change smoking habits or seating location as a result of the presence of the instrument system. Such changes could bias the data.

A number of studies have been published describing the measurement of concentrations of CO and nicotine in public and semi-public places. These data were interpreted in terms of exposure of the nonsmoker to cigarette smoke and in some cases were extended to include the effect of this exposure on the nonsmoker.

Carbon monoxide and nicotine were chosen as the tracers for analysis. They have been used in past studies because they represent reasonably specific trace materials for the gas and particulate phases of tobacco smoke.

Carbon monoxide is very stable in the atmosphere and is the second largest gas-phase constituent of cigarette smoke. It has been reported that there is an 80 percent correlation between CO and the particulate phase of mainstream cigarette smoke.

Nicotine is also stable in the atmosphere. It is the largest identifiable constituent of the particulate phase of cigarette smoke. In almost all locations, concentrations of nicotine can be specifically traced to tobacco smoke--the only other possible source being pesticide sprays. A 95 percent correlation between nicotine and the particulate phase of mainstream cigarette smoke has been reported.

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The purpose of this report is to document the reasons for selecting the analytical methods used and to report preliminary data that have been obtained using the system.

Therefore, this report will provide only a general description of the instrument system and its operation. An extensive discussion of these details is contained in a separate document, "Operation Manual for the Portable Air Sampling System," which has been furnished to the users of the system.

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II SUMMARY

A portable, unobtrusive instrumentation system for the measurement of carbon monoxide and nicotine in ambient air has been designed, built, and tested. It is shown in Figures 1 and 2. The portable instrument has the following specifications:

- Carbon Monoxide
  - Method: nondispersive infrared spectroscopy (NDIR).
  - Sensitivity: 0-50 ppm full scale.
  - Minimum detectable level: approximately 1 ppm.
  - Specificity: no known interferences that are not compensated.
  - Response time: approximately 10 seconds full scale.
  - Accuracy: linear to better than ±5 percent; absolute accuracy depends on calibration standards.
  - Resolution: data system resolution is 1 ppm.
- Nicotine
  - Method: gas chromatographic analysis of materials trapped on pretreated glass-fiber filters.
  - Sensitivity: 1-100 micrograms per cubic meter ($\mu g/m^3$).
  - Minimum detectible limits: 100 nanograms of nicotine, depending on the purity of the reagents and on the instrument background.
  - Specificity: no known interferences.
  - Sample time: 10 minutes to 1 hour.
  - Accuracy: better than ±10 percent at high concentrations; collection efficiency better than 90 percent; absolute accuracy depends on background levels.
- Power Source--Primary field power is two nickel-cadmium batteries that give approximately two hours of operating time. The system can operate indefinitely on either a 110 Vac power supply or a 12V automobile battery (through the cigarette lighter).
- Data Output--Data on CO concentration and air flow rate are printed on a paper tape using a modified hand calculator/printer. A microprocessor is used to give a running average of the CO concentration and flow rate.

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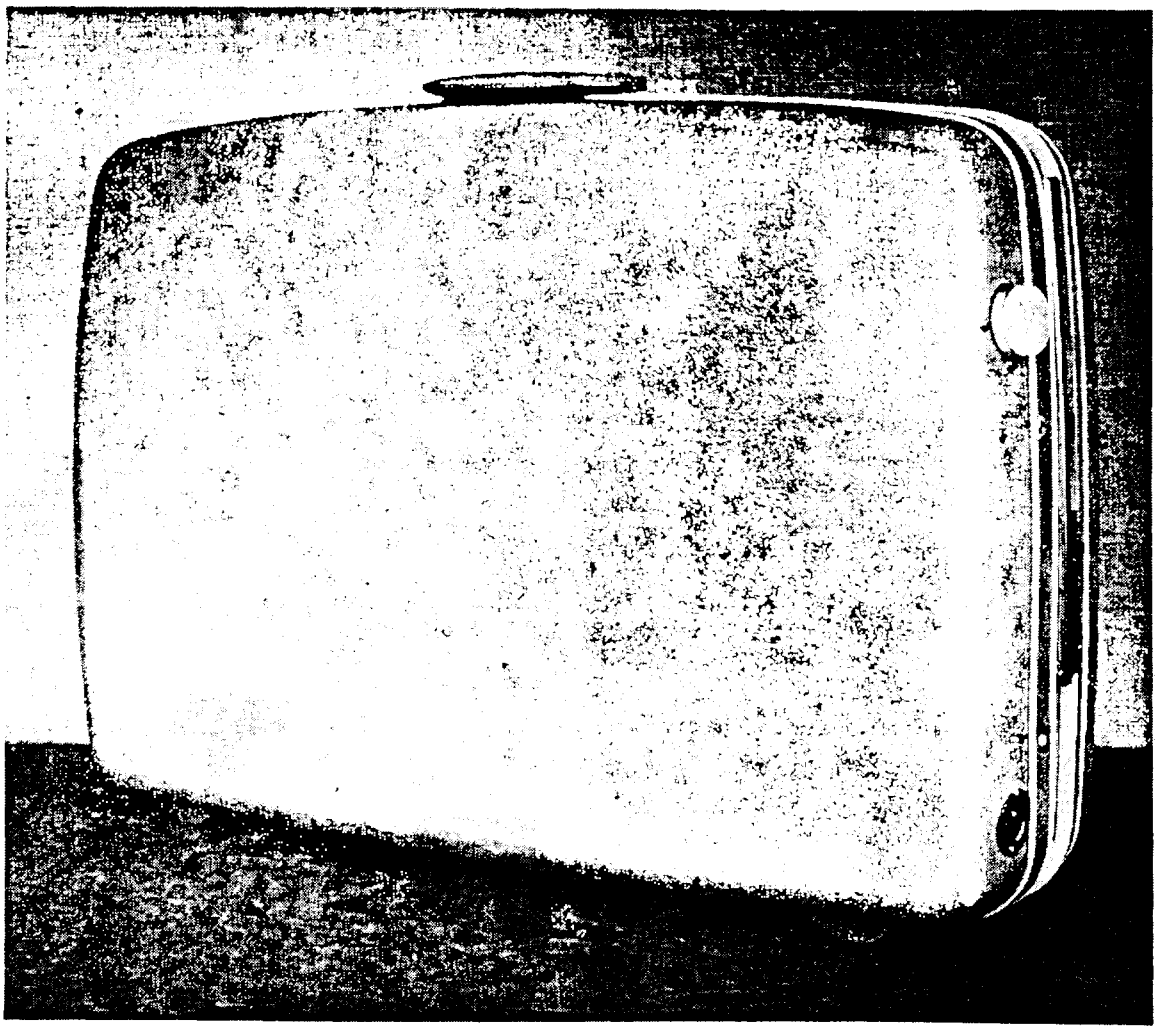

FIGURE 1 EXTERIOR OF PORTABLE INSTRUMENTATION SYSTEM

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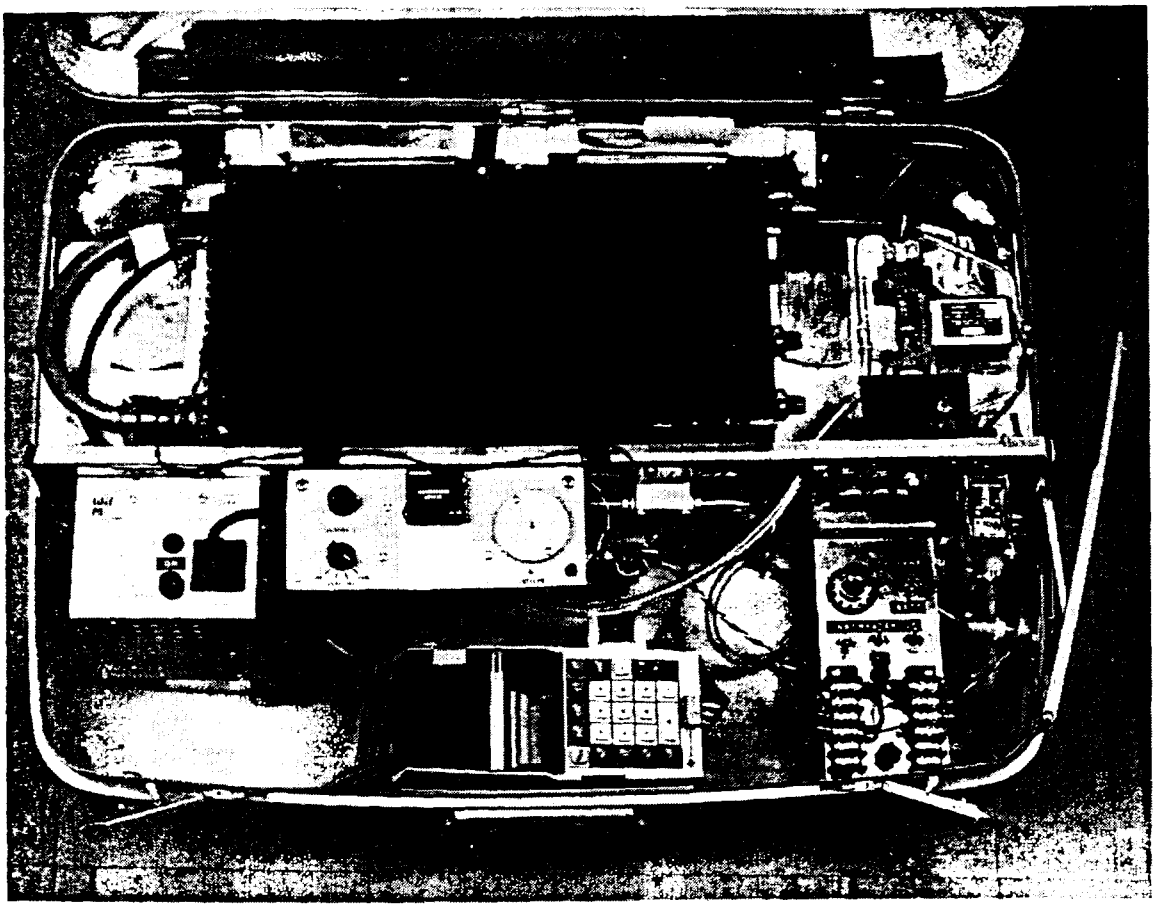

FIGURE 2 INTERIOR OF PORTABLE INSTRUMENTATION SYSTEM

- Size and Weight--The instrument system is mounted in a suitcase that has a built-in handle and wheels to facilitate transport. The suitcase is $29\frac{1}{2}$ in. × 21 in. × $9\frac{1}{2}$ in. and the system weighs approximately 60 lbs. Most of the weight of the system is from the batteries and the optical bench of the spectrometer.
- Field Test Results--The primary purpose of this program was to design and develop an instrument package, not to perform a field measurement program. However, sufficient field tests were performed to insure that the system was operating properly and that it could be used by technician-level personnel. Field tests were performed at seven locations:
  - A large auditorium
  - A large, well-ventilated corporate dining room
  - A beer hall/hamburger restaurant

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- A poorly ventilated, crowded bridge club
- A private bar
- A poorly ventilated bar
- The smoking car on a commuter train.

The measured CO levels were from less than 1 ppm to approximately 11 ppm. The measured nicotine levels were from 15 to 60 $\mu g/m^3$. The Occupational Safety and Health Administration (OSHA) and American Conference of Governmental Industrial Hygienists (ACGIH) 8-hour limits for CO and nicotine are 50 ppm and 500 $\mu g/m^3$, respectively.

Several attempts were made to incorporate an instrument system to determine the total suspended particulate concentration. All of these failed because it was not possible to develop an air sampling system that could sample the required air volume quietly enough to be unobtrusive.

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III ANALYSIS FOR CARBON MONOXIDE (CO)

One of the primary requirements of this program was to develop a portable instrument capable of producing the unimpeachable measurement of CO in the air. Therefore, at the start of the program all of the known analytical methods for measuring CO were reviewed to select the best method. The instruments utilizing this method were then evaluated to select the best instrument for use in the system. This instrument was then purchased and modified to conform to the exact requirements of the instrument system.

A. Regulatory Limits

The Environmental Protection Agency (EPA) standards for CO are:

- 10 mg/m^3 (9 ppm) maximum eight-hour time-weighted concentration not to be exceeded more than once a year.
- 40 mg/m^3 (35 ppm) maximum one-hour time-weighted concentration not to be exceeded more than once a year.

The OSHA and ACGIH limits are 50 ppm time-weighted 8-hour exposure.

Some data in the literature show concentrations as high as 90 ppm in indoor locations. For the purposes of the program, we assumed that the maximum measurement limit would be 100 ppm and that it is desirable to be able to measure down to 1 ppm. However, during validation field tests, we found that even under conditions of very heavy smoking the CO concentration was only 11 ppm. This finding was consistent with other test results reported in the literature with respect to the measurement of CO under realistic conditions. Hence, the final instrumentation sensitivity was set at 0-50 ppm on Range 1.

B. Analytical Methods for Carbon Monoxide

1. General

All regulatory limits for CO are specified in terms of time-weighted average concentration. Therefore, the instrument used to make the CO analysis must either be a true averaging instrument or it must have a sufficiently fast response time to measure rapid changes in CO concentration.

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For this program, we decided that the optimum approach would be to use a fast response time instrument and do the time-weighted averaging in the data system. This avoided the problem of proving that a CO analyzer had a time-weighted response.

The second advantage of a fast response time CO analyzer is that it provides some information on the possible variability of the nicotine concentration. For the nicotine measurement, a filter sample of the airborne particulate matter must be taken and analyzed later. The minimum time resolution of the nicotine measurement is about 10 minutes with the available air pump. It would be desirable to know the variation in nicotine concentration over a shorter time period than that. If it can be assumed that there is a local relationship between CO and nicotine, the short-term variability in the nicotine concentration can be inferred from variations in the CO concentration if the response of the CO analyzer is fast enough. Therefore, the optimum CO analysis would be fast (a few seconds response time), would give an analysis in real time, and would be easily portable.

During the development period, several different classes of analytical methods were reviewed to determine if they could meet these requirements. We evaluated the specifications for a number of instruments and contacted the instrument manufacturers. The final selection of the instrument to be incorporated into the instrument system was based on specificity, freedom from interferences, size, weight, complexity, and power requirements. The classes of instruments we considered are discussed below.

2. Direct Infrared Measurement of Carbon Monoxide

Carbon monoxide has a very distinctive spectra centered at about 4.66 μ. It consists of a group of very sharp, separated lines. This type of spectrum is ideal for infrared analysis, especially nondispersive infrared (NDIR). In fact, the EPA standard procedure for CO is an NDIR procedure.

NDIR instruments are fast, rugged, and reliable. The only significant interferences are from water vapor and CO_2, and these can be compensated for by using a standard compensation detector. Therefore, NDIR was selected as the method of choice for the measurement of CO.

The problem with this type of instrument is the requirement for a long-path optical cell to obtain the necessary sensitivity. A review of the manufacturers' specifications indicated that instruments with the necessary sensitivity are available. We evaluated several instruments ranging in cost from about $2,000 to $6,000 during this program.

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Two other types of infrared instruments might have been usable in this application: dispersive infrared instruments and infrared filter instruments. These two types of instrument were evaluated and rejected in favor of the NDIR method. The basis for this discussion will be discussed later.

3. Electrochemical Cell

In these devices, the CO diffuses from the atmosphere, through a semipermeable membrane, into a solid electrolyte where it is oxidized to CO_2. The output signal is an electric current proportional to the CO concentration. These devices are small, rugged, and require low energy. They generally cost less than $1,000.

One commercially available instrument that uses this method is the ECOLYZER, manufactured by Energetics Scientific Inc., New York. This instrument has been used to obtain some of the data on ambient CO concentration reported in the literature. We reviewed the manufacturer's literature to determine the specificity for the measurement of CO in ambient air. According to the manufacturer, a false reading of 1 ppm CO can be obtained from any of the following gases in air: C_2H_4, 1 ppm; C_2H_2, 0.3 ppm; SO_2, 100 ppm; H_2S, 100 ppm. In addition, the manufacturer states that unless a special filter is used, ethyl alcohol is also an interference.

This shows that some low molecular weight gases that are easily oxidized can give a false indication of the presence of CO. In bars or restaurants, the gases from stoves, cooking smoke, ethyl alcohol and body gases would all be expected to give false readings as CO if the ECOLYZER were used. Therefore, this method was rejected as not having unimpeachable specificity for CO.

4. Catalytic Oxidation

These devices utilize the heat of combustion of CO oxidation to CO_2 to raise the temperature of a small bead of catalyst. The output signal is a voltage proportional to the temperature of the catalyst bead. These devices have no inherent specificity for CO since any material that can oxidize on the catalyst surface, at its operating temperature, will be an interference. Therefore, these devices require an efficient series of filters on the inlet air to remove these interferences. They have adequate sensitivity and speed of response, but the lack of specificity makes this method unacceptable in this application.

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5. Colorimetry

Commercial devices are available that utilize a color-forming reaction between CO and a special test paper. Air is pulled through the paper tape for a specified period of time and the color formed is read automatically by a photo cell.

These devices are small and sufficiently sensitive for the application but they are quite slow. In addition, the commercially available instrument is significantly larger than the NDIR.

6. Gas Chromatography

As a laboratory instrument, gas chromatography is second only to NDIR as the instrument of choice for the analysis of CO. However, as a portable field instrument its complexity, size, and cost rank below NDIR.

7. Other Methods of Analysis

We performed a preliminary evaluation of several other methods of analysis for CO. All of the following methods were excluded from further consideration for this instrument system because of one or more of the following reasons: lack of specificity, requirement for liquid handling, cost, or slow speed of response. The methods evaluated were:

- Amperometric analysis
- Bioluminescence
- Dual isotope NDIR
- Mercury substitution ultraviolet analysis.

C. Selection of Infrared Instrument

As discussed in the previous section, infrared analysis was selected as the analytical method of choice primarily because of its specificity, potential speed, and sensitivity.

There are three different types of infrared instruments: dispersive instruments that use gratings or prisms, filter instruments, and non-dispersive instruments (NDIR).

Dispersive instruments were eliminated because no small, portable prism or grating instrument that had long sample cells could be located.

A filter instrument (Wilks, Miran) was obtained on loan from the manufacturer and tested for this application. The size and sensitivity were more than adequate; however, water vapor and CO_2 absorb in the same

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spectral region as CO. Therefore, it would have been necessary to remove both water and CO_2 from the sample air. This would have required a two-stage filter and a much larger air pump.

The instrument of choice was an NDIR instrument. There are at least 40 different models of NDIR available. Most of these instruments are designed to measure the CO in auto exhaust and do not have the required sensitivity. Of those with the required sensitivity (Beckman, Bendix, Horiba, Infrared Industries, Mine Safety Appliances) the Horiba AIA-24 is the only one that is small, relatively light weight, has the optical bench physically separated from the electronics, uses a LUFF detector, and incorporates a separate interference detector to compensate for water vapor and CO_2. Moreover, the Horiba is proven in the field and serves as the basis for an EPA approved instrument. After a thorough evaluation, we bought this instrument for use in the portable system.

1. Modification of the Horiba AIA-24

There are no portable, battery-operated NDIR instruments available with the required sensitivity. Therefore, it was necessary to modify the AIA-24 (which was designed for 110-Vac operation) to operate on 12-V batteries. This modification involved the removal of three heaters, installation of insulation, shortening of the optical bench, and installation of a special voltage regulator on the infrared sources. The result was a reduction of required power from 220 watts to 28 watts. This made it possible to operate the instrument from batteries for a useful period of time. The drawback of the modification was the requirement of a long warm-up time; at least 45 minutes. Fortunately, the warm-up can be performed using a power supply other than that of the built-in batteries. Once the system is fully warmed-up, the built-in batteries are sufficient for a 2-hour test period. The details of this modification are discussed in the operations manual for the sampling system.

2. Sensitivity

The original sensitivity of the AIA-24 was 0-25 ppm. This has been changed to 0-50 ppm, with switch-selectable ranges of 0-100, 0-250, and 0-500 ppm also available.

This instrument has been calibrated using a dynamic dilution system and has been found to be linear over the range 0-100 ppm.

3. Response Time

The air flow rate through the instrument is approximately 4.2 l/min. The cell volume is approximately 200 cc so the sample air is changed every three seconds. The electronic response time (to 90 percent of the maximum value) is approximately 10 seconds, which limits the output response to 10 seconds.

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There is a digital integrator in the data system that has switch-selectable averaging times of 5, 10, and 20 seconds and 1, 2, 5, and 10 minutes. The data printed out at these rates represent the average of measurements made twice a second.

4. Specificity

Because of the nature of the detector used in this instrument, the only known interferences for the measurement of CO are CO_2 and water vapor. The sensitivity to these gases is compensated for through the use of a standard compensation detector furnished by the manufacturer. When the instrument is properly adjusted, a change from dry air to 100 percent saturated air gives a response of less than 2 ppm as CO.

5. Calibration

The instrument is calibrated using certified zero-air and CO standard gases. These are blended by the manufacturer and then analyzed by comparison with reference standards. The standard gases used by SRI have also been checked by the State of California against its primary standards. Concentrations of 9.6, 25.2, 40.1, and 75.0 ppm were used to set the calibrations and to check the linearity of the instrument. The linearity and accuracy were both better than ±5 percent over this range.

6. Resolution

The data system was designed to round-off to the nearest 1 ppm to eliminate the problem of having data with more significant figures than are justified.

7. Packaging

The instrument system is built into a suitcase as shown in Figures 1 and 2. The suitcase is $29\frac{1}{2}$ in. × 21 in. × $9\frac{1}{2}$ in. and the system weighs about 60 lbs. It has a built-in handle and wheels to make it easier to move. The only external evidence of the instrument system is the filter socket and the "operate" switch in the side of the suitcase. The filter holder cannot be hidden because it is necessary to have the filter surface exposed to the air for valid particulate sampling.

The "operate" switch is located under the extension handle that is used to move the suitcase, so it is effectively hidden.

Most of the weight of the instrument system is in the nickel-cadmium batteries and the optical bench for the NDIR. This weight is unavoidable if the specifications for the instrument are to be met.

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IV NICOTINE MEASUREMENT

A. Measurement Limit

A review of the literature showed that reported nicotine concentrations range from 0.7 to 35 $\mu g/m^3$ in public and semi-public places. For the purposes of this work, we assumed that the maximum nicotine concentration that will be encountered is 100 $\mu g/m^3$. We also assumed that the system should be able to measure 1 $\mu g/m^3$ of nicotine with an accuracy of ±20 percent or better.

B. Feasibility of Direct Measurement of Nicotine in Air

The vapor pressure of nicotine at ambient temperatures will be so low that any direct measurement in the vapor phase will not be possible without the use of very long path cells.

A survey of the literature indicated that essentially all the nicotine from tobacco smoke is present in the particulate phase. The only feasible direct method of measuring the nicotine concentration of smoke particles is through the use of some form of spectroscopic analysis, probably infrared. It is theoretically possible that an instrument could be developed to analyze individual smoke particles for nicotine. However, to our knowledge, such an instrument has not been constructed and, if it were, it probably would not be portable. In addition, the presence of other particulate matter in the smoke particles will make the individual particles optically dense with little penetration of the analyzing radiation. Therefore, we conclude that, while real-time detection of nicotine in smoke particles may be possible, it was not a practical method to pursue in this study. Consequently, we developed a method in which air sample is pulled through a filter to trap the nicotine and the filter is then returned to a laboratory for analysis.

C. Air-Sampling System

After evaluation of a number of different types of filters, including such materials as Poropak and Tenax, we selected Gelman type AE glass-fiber filters. This selection was made because of the requirement for stability against strong acids, very low flow-resistance, and excellent trapping capability for very fine particles.

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Laboratory tests at SRI (see Appendix A) showed that nicotine breakthrough occurred after about 10 minutes with untreated filters. Therefore, we developed and validated a pretreatment procedure. Each filter was spiked with 0.4 ml of 0.5 M $KHSO_4$ and dried for two hours at 90°C. The pretreated filters were tested by sampling air from a smoke chamber for one hour. The flow was 4 l/min and the nicotine concentration was 275 $\mu g/m^3$. No breakthrough was observed. These filters will be hygroscopic above 86 percent relative humidity so field tests should be limited to conditions dryer than that.

The filters are 37 mm in diameter and are held in special plastic filter holders that can be sealed before and after use. During tests the filter holder is open so the entire face of the filter is exposed to the air. The filter holder can either be placed in a socket in the side of the suitcase or an extension can be used to place it at some other desired location (e.g., on a table).

To make a quantitative determination of the concentration of nicotine in the air it is necessary to know the volume of air sampled by the filter. This is done using a hot-wire anemometer in the air line between the filter socket and the air pump. The flow meter gives a continuous measurement of the air flow rate during the sampling period.

Several different air pumps were evaluated. The Brailsford model TD-4X2S double-acting pump was selected because it has an adequate flow rate (4 l/min) through the filter, is lightweight and quiet, and is very efficient electrically. We would have preferred to have a greater pump capacity to get larger samples for the nicotine analysis, but a better pump could not be found.

The air from the nicotine sampling system is exhausted into the CO analyzer, so a single pump provides the air for both the CO and nicotine analysis.

D. Analytical Procedure for Nicotine

The measurement of ambient nicotine concentration requires an accurate, specific analysis technique to determine the concentration of nicotine in the presence of unknown interferences. In general, the system should avoid the requirement for extensive equipment or esoteric techniques that would not normally be available in a modern analytical laboratory.

A review of the literature and discussions with SRI personnel led to the conclusion that there is nothing sufficiently unique about nicotine chemistry to permit specific measurement without prior separation or concentration from gross samples taken from the atmosphere. Separation or concentration could be performed in a number of ways, but all separation and concentration techniques require sample handling that would not

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be practical to perform in a portable package. Therefore, the only way that unimpeachable concentration data can be obtained for this compound is to collect the smoke on filters and then return these filters to a laboratory for analysis. Consequently, the nicotine concentration will not be determined in real time.

The filters are returned to the laboratory, extracted, and analyzed using gas chromotography. An easily identifiable internal standard (quinoline) is utilized during the extraction procedure to allow calculation of the initial amount of nicotine collected on the filter.

We have performed a preliminary analysis of a number of other potential analytical methods for determining nicotine in cigarette smoke. All these methods fail to meet one or more of the requirements for a highly specific, extremely sensitive, fast, and accurate test for nicotine. These methods include:

- Liquid chromatography
- Thin-layer or paper chromatography
- Plasma chromatography
- Infrared analysis
- Ultraviolet analysis
- Laser spectroscopy
- Nuclear magnetic-resonance spectroscopy
- Electron paramagnetic-resonance spectroscopy
- Paper or liquid colorimetry
- Radioimmunoassay
- Immunoassay
- Bioluminescence.

1. Extraction Procedure

The following is an outline of the extraction procedure. Complete details of this procedure are given in the operations manual for the sampling system.

(1) Place the filter in a 60-ml separatory funnel.

(2) Spike the filter with a known amount of quinoline/benzene solution.

(3) Acidify with 5 ml 0.5M H_2SO_4.

(4) Extract 3 times with 10-ml aliquots of methylene chloride.

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(5) Strip the acid of all remaining methylene chloride using a nitrogen flush.

(6) Transfer the acid to 10-ml volumetric flask.

(7) Add 2.5 gm of NaCl.

(8) Add 1 ml of 10N NaOH.

(9) Add enough water to make up 10 ml of solution.

(10) Extract with 100 µl of benzene.

(11) Inject 5 µl of benzene into the gas chromatograph.

2. Gas Chromatograph Column

The selection of an appropriate column for the gas chromatography of trace levels of nicotine is essential. Several column packings (e.g., FFAP, OV-210, and OV-101) that work well at higher concentrations of nicotine tail badly or show no response at all to an injection of 10 ng of nicotine. A suitable packing is 5 percent Carbowax 20M and 2 percent KOH on Chrom W, AW-DMCS, on which an injection of 5 ng of nicotine gives a good peak shape. The column used was 6 ft × 2 mm internal diameter. It was run isothermally at 130°C with a helium carrier at 30 cc/min.

Under these conditions, the retention time for nicotine was 9.2 min and the retention time for quinoline was 12.0 min with no overlaps between the peaks.

3. Detectors

An alkali flame detector, in the nitrogen-specific mode, could have been used on the gas chromatograph to further improve the specificity for nicotine and to discriminate against most of the interferences. However, because of our in-house experience, we chose to use a gas chromatograph equipped with a commercially available nitrogen-specific electrolitic conductivity detector (invented by Dr. Coulson of SRI).

In this detector the effluent stream from the gas chromatographic column is delivered into a high-temperature microtube furnace fitted with a quartz tube in which the components eluted from the column are hydrogenated over a hot nickel catalyst. The products of hydrogenation are contacted with an acid adsorption packing that removes H_2S and hydrogen halides. The resulting gas stream, containing NH_3 from the hydrogenation of the organic nitrogen, is then passed through an electrolytic conductivity detector cell. This detection system is insensitive to aliphatic and aromatic hydrocarbons, ketones, alcohols, and sulfur-, phosphorus-, and halogen-containing compounds. It also gives equal response to all types of organic nitrogen and is sensitive to as little as one nanogram of organic nitrogen.

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A gas chromatograph with a nitrogen-specific conductivity cell as a detector has a very low probability of having interferences that will affect the "nicotine peak." However, in view of the requirement for unimpeachable data, we ran some experiments using SRI's gas chromatograph/mass spectrometer. These provided an unequivocal analysis of the nicotine peak to be certain that it was only nicotine and did not contain any interferences. The samples for these validation tests were actual field samples from public and semi-public places.

The instrument used for the GC/MS analysis was a Finnigan Model 3200 GC/MS equipped with a Model 6100 data system. The technique of mass fragmentography (specific ion detection) was used to achieve the necessary sensitivity and specificity. In mass fragmentography, the mass spectrometer is made to look at only specific ions instead of scanning the entire mass range. The mass peaks monitored were 129, 133, 161, and 162. Mass 129 is the base peak and molecular weight of quinoline, and it was used as an internal standard. Masses 133, 161, and 162 were representative of nicotine. Mass 133 was used for quantification unless there was interference, then mass 161 and 162 were used. Mass 84, the base peak of nicotine, was not monitored because of interferences and a high background level.

Our conclusion was that the nitrogen-specific detector is a satisfactory device for the analysis of nicotine and that it has a very low probability of interference from other compounds. However, completely unambiguous data can be obtained only by using a mass spectrometer as a detector.

4. Calibration

The calibration of the gas chromatograph was performed by injecting aliquots of known concentration of nicotine and quinoline dissolved in benzene, the same solvent used for the final extraction. The area under each peak was calculated using an automatic electronic integrator. The area for each peak was plotted against the known amount of each compound injected. We found that both detectors were linear to better than ±3 percent over the entire calibration range (to 1000-ng injection).

5. Data Reduction

A known amount of quinoline was spiked onto each filter at the start of the extraction procedure. The assumptions made were that:

- The instrument sensitivity-ratio remains constant (true for all modern gas chromatographs).
- The extraction efficiency and stability are the same for nicotine and quinoline.

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Therefore, the amount of nicotine originally on the filter could be calculated by the following equation:

$$N_f = Q_s \frac{A_n}{A_q(1.57)}$$

where:

Q_s = weight of quinoline spiked on the filter

A_n = area of chromatograph peak for nicotine

A_q = area of chromatograph peak for quinoline

N_f = weight of nicotine on the extracted filter.

The instrument sensitivity ratio (the 1.57) is the relative instrumental sensitivity to nicotine and quinoline. This constant will change depending on the calibration of the instrument used to make the analyses. The use of quinoline as an internal standard eliminates the need for knowing the exact extraction efficiency of the procedure.

6. Accuracy

The accuracy of the analytical procedure is dependent upon how well the laboratory techniques are performed. With good technique and carefull handling of all the agents, glassware, and standards, the nicotine analysis should have an accuracy of ±5 percent or better.

7. Sensitivity

The minimum detectable amount of nicotine is about 1 ng. Therefore, for ±20 percent accuracy at least 5 ng of nicotine should be in the 5 µl of benzene injected into the gas chromatograph. Since the 5 µl aliquot is 1/20 of the total amount of benzene used for the final extraction, about 100 ng of nicotine must be extracted from the filter. At a concentration of 1 $\mu g/m^3$, this requires an air sample of 100 liters. If the sample pump is capable of pumping at 4 l/min, this will require a 25-min sampling time. Thus, the requirement for 100 ng of nicotine on the filter sets a minimum sampling time at low ambient concentrations of nicotine.

8. Background

We found that most reagents used in the analytical procedure were contaminated with nicotine, even though fresh bottles of the best available materials were used. This contamination was equivalent to about 25 ng of nicotine on the filter. To compensate for the contamination,

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blanks were always run with each set of samples. It was also necessary to use very good laboratory technique so all samples would be treated in the same way with the same amount of reagents.

It must be stressed that the nicotine contamination levels are very small (many orders of magnitude below the toxic level). They are significant only because of the extreme sensitivity of the method and the small size of the nicotine sample obtained in the short sampling time.

9. Specificity

The same gas chromatograph column was used for both the mass spectrometer and the nitrogen-specific detector. In the limited number of "real world" samples that we analyzed using the gas chromatograph, we did not find any significant contamination of nicotine peaks that could not be corrected. Therefore, we believe that the mass spectometer, as a detector for nicotine, is unambiguously specific.

The nitrogen-specific detector was used for the filter breakthrough test and for analysis of a limited number of field samples. We did not find any evidence of contamination of the nicotine peak in either set of tests. However, we did not perform a complete validation of this procedure, so we cannot be sure that it is unambiguously specific for nicotine.

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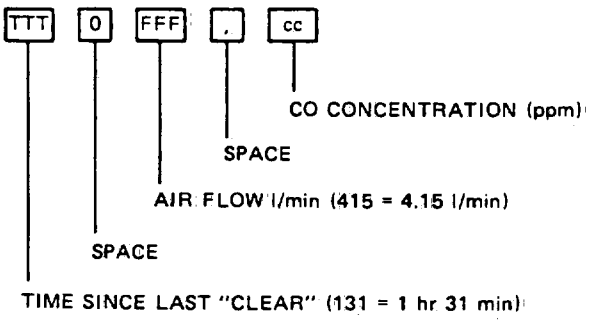
V DATA SYSTEM

The built-in data system converts the analog voltage outputs from the flow meter and the CO analyzer to time-integrated flow rates and concentrations. These are printed on a paper tape along with time from the start of sampling.

The data system uses commercially available integrated circuits to perform all of the data processing and a slightly modified Texas Instruments 5050M calculator/printer to print out the data. Complete details of the data system are given in the operating manual for the sampling system.

The integration time (and data printout intervals) can be selected from seven different time periods between 5 seconds and 10 minutes. During these time periods, the data sampling rate is approximately two samples per second, so variations in CO concentrations as short as a few seconds can be accurately integrated.

The data format is:



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VI POWER SOURCES

The instrument was designed to operate from both self-contained batteries (for at least two hours) and normal 115-Vac power. Table 1 shows a variety of battery types that were evaluated for use in the instrument system.

Table 1

COMPARISON OF BATTERIES

Battery Type	Watt-Hours/Pound	Recharge Cycle
Silver oxide	50-70	--
Lithium	100-150	--
Mercury	46	--
Alkaline	20-35	--
Nickel-cadmium	12-16	500-2000
Lead-acid (gel)	9	200-500
Silver-cadmium	22-34	150-300
Silver-zinc	40-50	80-100

The first four types listed are primary (nonrechargeable) batteries and are generally considerably more expensive than the last four types, which are rechargeable (secondary) batteries. The major advantage of the primary batteries is their lower weight for a given energy capacity. However, for the purposes of this system, the rechargeable batteries will be less expensive in the long run, even though they do require recharging between tests.

Of the rechargeable batteries, the nickel-cadmium type was selected because it has a significantly better power/weight ratio than the lead-acid type and is much less expensive than the silver batteries. Also, nickel-cadmium batteries with the necessary power ratings are commercially available.

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Two other power systems are also provided. The entire data system operates on 12 Vdc, so an extension cord is supplied that allows the system to be plugged into the cigarette lighter of the vehicle in which it is being transported. This gives almost unlimited operational and stand-by time. Also, a 110-Vac to 12-Vdc power supply is furnished to allow the system to operate off "wall power." This is the normal mode for warm-up and can be used for field measurement whenever the power is available and conditions warrant it.

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VII PARTICULATE ANALYSIS

Originally we proposed to include a system for making total suspended particulate (TSP) measurements. This was to be done by sampling air through a large diameter filter (115 mm) and weighing the filter before and after sampling.

The accuracy of repeated weighings of the filter used for the TSP measurements was about ±10 µg per weighing, so the total weighing accuracy was about ±20 µg. Therefore, a total particulate weight of 200 µg could be measured with an accuracy of ±10 percent (±20 µg). The accuracy of data obtained during field testing, therefore, depended upon the weight of the material collected.

To collect 200 µg in a relatively clean atmosphere (50 $\mu g/m^3$), it is necessary to sample 4 m^3 of air. This proved extremely difficult to do and still meet the collateral requirements of quiet, unobtrusive operation. Several approaches were tried and were found unsuccessful.

The best available pump was a modified Rotron pump that could sample at 70 l/min (2.4 ft^3/min) with a vacuum of approximately 7 inches of water on the filter. Using this pump, the minimum sampling time would have been 57 minutes. Thus, it would have been marginally adequate for the job. However, it was far too noisy for unobtrusive operation in any but the noisiest location. It sounded like a small vacuum cleaner, which it essentially was. Because of these problems, the attempt to include TSP measurements in the instrument system was abandoned.

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VIII RESULTS OF FIELD TESTS

The primary purpose of this program was to design and develop an instrument system, not to perform a field measurement program. However, a limited number of field tests were performed using the instrument system. The purpose of these tests was to ensure that the system was operating properly, to show that it could be operated by technician level personnel, and to develop the basic testing protocol.

There have been some very high values of CO reported in the literature and it was necessary to ensure that the instrument system could cover the concentration range that we expected to encounter in field tests. One particular test location (the bridge club) was selected because of the large number of smokers present.

To put the following results in context, note that the Occupational Safety and Health Administration (OSHA) and the American Conference of Governmental Industrial Hygienists (ACGIH) 8-hour limit for CO is 50 ppm. The limit for nicotine is 500 $\mu g/m^3$.

A. Tests with Untreated Filters

The first four field tests were performed before we found that there could be nicotine breakthrough on untreated filters. Therefore, the nicotine measurements made during these tests are suspect and will not be reported. However, the CO values are reliable data. The four sites tested were:

- A large auditorium at SRI
- A large, well-ventilated dining room at SRI
- A beer hall/hamburger restaurant
- A poorly ventilated, crowded bridge club.

1. SRI Auditorium

This was the first test of the system. The test was interrupted and no data were obtained because the people present in the auditorium complained about the noise from the TSP sampler. This sampler was subsequently removed from the system because the noise problem could not be solved.

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2. SRI Dining Room

This is a large, well-ventilated dining room that has separate seating for smokers and nonsmokers. The test was performed for an hour and a half in the smoking section. Unfortunately, there were very few smokers present during the test period. The data show less than 1 ppm CO during the entire period. However, the test did show that the system could be operated unobtrusively for an extended period of time.

3. The Oasis

The Oasis is a popular beer hall/hamburger restaurant that has only natural ventilation (except for the hoods over the grills). There is one large door and a few small windows. The test was performed for a period of 1 1/2 hours during lunch time when it was quite crowded. The test team estimated that approximately 10 percent of the people were smoking (3-5 out of a total of 30-50 at any given time). Most of the CO readings were less than 2 ppm. There was a 2 minute period when the concentration rose to 3-4 ppm and another period of a few seconds when the peak concentration rose to 18 ppm.

This test shows that the system was performing well and that it could operate unobtrusively in a crowded environment. It also indicated that there were no significant false CO readings from the volatile products from beer.

4. The Bridge Club

This test was performed at a commercially operated bridge club where the players paid an admission fee. The room was approximately 30 feet by 75 feet with 24 tables, all of which were full. Unfortunately, the physical arrangement of the room and the lighting made it impossible to be unobtrusive. However, after the first few minutes we were mostly ignored and in our opinion the data were not compromised by people standing near us.

The room had very poor ventilation. There was one door open at the far end of the room and a window approximately 25 feet from the sampling site was opened after two hours and fifteen minutes of play. There was a ventilation system in the ceiling but it did not appear to be working. The paper tassels hanging from the ceiling showed very little movement.

This site was selected because a member of the SRI staff, who was a consultant on the project, complained about the "extremely smokey" conditions. The club has subsequently moved to new quarters because of complaints by the players regarding air quality.

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We arranged to have the ash trays emptied into cans that we supplied so we obtained an accurate count of the number of cigarettes smoked. Approximately 400 cigarettes were smoked over a four-hour period. There were 100 people and we estimate that 20 to 25 percent were smoking at any given time.

The data on CO concentration are shown in Figure 3. There was a gradual buildup of CO over the first 3 1/2 hours to a maximum of 11 ppm. At that time, approximately 1/3 of the people left and the CO concentration remained at 11 ppm. The leveling off of the CO concentration may have resulted from the combination of ventilation caused by the movement of people through the doors and the reduced number of smokers.

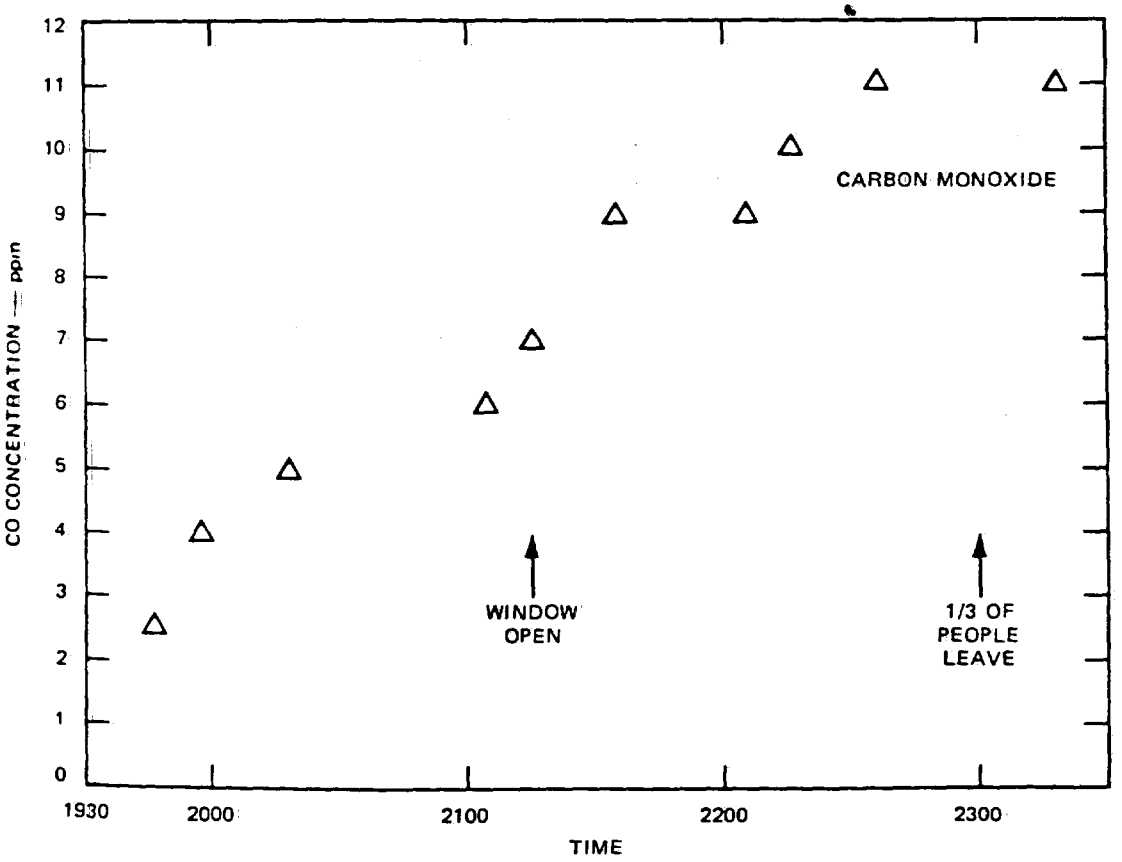

FIGURE 3 CO DATA FROM BRIDGE CLUB TEST

The opening of the window (after 2 hours and 15 minutes of play) did not appear to change the rate of CO buildup. However, there was no wind outside to cause ventilation between the open door and the open window.

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The calibration of the CO analyzer was checked before and after the test and was found to be accurate.

This test was performed under very smokey conditions. There was obvious reduction in visibility within the length of the room and there were numerous complaints by the players. However, even under these conditions we measured a maximum of 11 ppm of CO.

B. Tests with Treated Filters

The last three tests were performed using $KHSO_4$ treated filters, so both CO and nicotine data are available. The sites were:

- A private bar/restaurant
- A public bar
- The smoking car on a commuter train.

1. A Bar/Restaurant

The bar area of a private bar/restaurant was used as the test location. This bar area is 100 feet by 50 feet. At one end, it is open to a large dining area. The test team sat at a table near the center of the bar.

The test was conducted for 55 minutes using a $KHSO_4$-treated filter. There were 16 to 18 people present and most smoked during the test period. The average nicotine concentration was 16.3 $\mu g/m^3$. The CO concentration was about 1 ppm, with a 2 ppm maximum that lasted for 2 minutes.

There was no advance notification to the management and no one paid any attention to the test team or the test equipment.

2. The Brass Rail

The Brass Rail is a popular bar in an industrial area. It is about 70 ft by 40 ft with poor ventilation. The test crew sat at the bar. The test duration was 61 minutes with a $KHSO_4$-treated filter.

There were 45 to 75 people present with 15 to 20 smoking at any given time. The measured average nicotine was 60 $\mu g/m^3$. The average CO concentration was 2 ppm, with a maximum of 4 ppm for 5 minutes.

No advance arrangement was made with the management and no one paid any attention to the test team.

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3. A Railroad Car

The commuter trains on the San Francisco Peninsula always have at least one smoking car. A test was performed in one of these cars during its run from San Jose to San Francisco. It departed at 7:17 am and arrived at 8:40 am. There were between 8 and 69 people in the car, with approximately half smoking at any time. It was an old car with poor ventilation.

Three treated filters were exposed sequentially for 10 minutes, 20 minutes, and 40 minutes, respectively. The measured nicotine concentrations were 33.2, 21.2, and 45.8 $\mu g/m^3$, respectively.

The CO concentrations showed large and rapid variations (from 13 ppm to 5 ppm in one minute). There was not sufficient ventilation to make these variations reasonable. We concluded that the CO readings were being influenced by the high degree of vibration and motion of the car. Therefore, no CO readings are reported.

No advance arrangements were made with the railroad and no questions were asked by the train crew.

C. Conclusions

As a result of these field tests we conclude that the instrument system can make real-time measurement of CO and can take samples for determining nicotine concentration while being operated unobtrusively. However, it was not possible to make unobtrusive measurements of the total suspended particulate matter.

The range and sensitivity of the CO analyzer was satisfactory for the concentrations that we observed. The observed range was 1 to 11 ppm.

The filter pretreatment procedure, the sampling procedure, and the analysis procedure for nicotine was satisfactory for the concentrations that we observed. The observed range was 15 to 60 $\mu g/m^3$.

All of these tests were performed by technicians with a minimum amount of training on the system. Therefore, we conclude that the system can meet the desired specifications when operated by trained technicians.

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Appendix A

VALIDATION OF FILTER PRETREATMENT PROCEDURE

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Appendix A

VALIDATION OF FILTER PRETREATMENT PROCEDURE

To ensure that the nicotine values were experimentally valid, it was necessary to test the possibility that there might be breakthrough of nicotine from the filter. If breakthrough occurred, it would require pretreatment of the filter to ensure that all nicotine is trapped on the filter.

The breakthrough tests consisted of placing two filters in series and pulling air through both of them using the Brailford pump in the instrument system. A box was set up with a blower moving 60 ft^3/min of air into the box. Lighted cigarettes were placed in the end of the box nearest the blower and the filters were placed in the opening at the other end of the box where the smokey air exited.

The results of these tests are given in Table A-1. The first filter was treated with 0.4 ml of the solution shown in the table. In all cases, the second filter (which was used to detect any nicotine that escaped the first filter) was treated with 0.4 ml of 0.5M H_2SO4. After treatment, the filters were dried for 2 hours at 90°C.

The nicotine concentration was about 275 $\mu g/m^3$, so this was a very severe test for capture efficiency. The efficiency figures were calculated by dividing the amount of nicotine on the first filter by the total nicotine on the first and second filters.

Three conclusions can be reached from these data:

- Plain (untreated) filters are not satisfactory for sampling high concentration side-stream smoke even for 10-minute sampling time.
- For up to 30 minutes, it is probably satisfactory to use filters treated with 0.05M $KHSO_4$ or 0.05M H_2SO_4 for 90+ percent capture efficiency.
- For 60 minute sampling it is necessary to use 0.5M $KHSO_4$ or 0.5M H_2SO_4 to get good capture efficiency.

There is essentially no difference in flow rate (pressure drop) between the 0.05M and the 0.5M treated filters, so there is no reason for not using the 0.5M treatment.

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Table A-1

FILTER PRETREATMENT VALIDATION TESTS

Test Number	Time (min)	First Filter	First Filter Efficiency (%)
1	10	Plain	15
2	10	0.05 M H_2SO_4	98
3	10	0.05 M $KHSO_4$	99
4	30	Plain	--*
5	30	0.05 M H_2SO_4	95
6	30	0.05 M $KHSO_4$	90
7	60	0.05 M $KHSO_4$	61
8	60	0.05 M H_2SO_4	35
9	30	0.5 M $KHSO_4$	99
10	60	0.5 M $KHSO_4$	99
11	60	0.5 M H_2SO_4	99

*Test not performed because of breakthrough at 10 minutes.

We recommended the $KHSO_4$ treatment in the operations manual because this chemical is not hygroscopic below 86 percent relative humidity, so the filters will remain dry up to that value. The H_2SO_4-treated filters, however, are hygroscopic at all normal relative humidities. Therefore, the percentage of moisture in H_2SO_4-treated filters will change and cannot be predicted

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